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| (54) Title: FUNCTIONALIZED INITIATORS FOR ANIONIC POLYMERIZATION (57) Abstract A process for the preparation of hydrocarbon solutions of monofunctional ether initiators of the following general structure: M-Z-O-C(R ¹ R ² R ³) wherein M is an alkali metal; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; and R ¹ , R ² and R ³ are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, and their employment as initiators in the anionic polymerization of olefin containing monomers in an inert, hydrocarbon solvent comprising reacting an omega-protected-1-haloalkyl with lithium metal dispersion having a particle size between 10 and 300 millimicrons in size, at a temperature between 35 and 130 °C in an alkane solvent containing 5 to 10 carbon atoms. | | |

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FUNCTIONALIZED INITIATORS FOR ANIONIC POLYMERIZATION

This invention concerns novel anionic initiators for use in
 5 polymerizing olefinic-containing monomers, a process for making the
 anionic initiators, a process for the polymerization of olefinic-containing
 monomers using the anionic initiators of this invention and polymers
 produced by this polymerization process.

Useful polymeric products are obtained by polymerizing olefinic-
 10 containing monomers in the presence of an organo-alkali metal initiator
 and subsequently reacting the resulting polymer, containing an active
 alkali metal end group or groups, with a reagent which will couple the
 polymer molecules or replace the alkali metal with more stable reactive
 end groups.

Monofunctional silyl ether initiators, containing alkali metal end
 15 groups useful in effecting such polymerization reactions are disclosed in
 Great Britain published patent application 2,241,239, published August 28,
 1991. These monofunctional silyl ether initiators were demonstrated to be
 useful in producing polydienes having desirable characteristics such as a
 20 molecular weight of typically 1,000 to 10,000, 1-4 content of typically 90%,
 etc.

Although analogous lithiohydrocarbyl ether compounds have been
 prepared and utilized in organic syntheses by M. Gardette et al,
 Tetrahedron, 41, 5887 [1985], these were prepared in ethereal solvents
 25 only, wherein their stability was poor and their utility as polymer initiators
 disadvantageous because of high solvent polarity.

The present invention provides a process for the preparation of
 novel, hydrocarbon solutions of monofunctional ether initiators of the
 following general structure:

30



wherein M is defined as an alkali metal, preferably lithium; Z is a branched
 or straight chain hydrocarbon tether group which contains 3-25 carbon
 35 atoms, optionally containing aryl or substituted aryl groups; and R¹R² and

R^3 are independently defined as H, alkyl, substituted alkyl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, and their employment as initiators in the anionic polymerization of olefin containing monomers in an inert, hydrocarbon solvent, optionally containing a Lewis Base. The process reacts selected protected omega-protected-1-haloalkyls whose alkyl groups contain 3 to 25 carbon atoms, which are reacted with lithium metal in a liquid alkane, cycloalkane or aryl solvent, at a temperature between about 35° C and about 130° C.

The initiator precursor omega-protected 1-haloalkyls (halides) are prepared from the corresponding haloalcohol by the standard literature methods. For example, 3-(1,1-dimethylethoxy)-1-chloropropane is synthesized by the reaction of 3-chloro-1-propanol with 2-methylpropene according to the method of A. Alexakis, M. Gardette, and S. Colin, Tetrahedron Letters, 29, 1988, 2951. The method of B. Figadere, X. Franck and A. Cave, Tetrahedron Letters, 34, 1993, 5893, which involved the reaction of the appropriate alcohol with 2-methyl-2-butene catalyzed by boron trifluoride etherate is employed for the preparation of the t-amyl ethers. The triphenylmethyl protected compounds, for example 3-(triphenylmethoxy)-1-chloropropane, are prepared by the reaction of the haloalcohol with triphenylmethylchloride, according to the method of S. K. Chaudhary and O. Hernandez, Tetrahedron Letters, 1979, 95. The compound 4-(methoxy)-1-chlorobutane, and the higher analogues, are synthesized by the ring opening reaction of tetrahydrofuran with thionyl chloride and methanol, according to the procedure of T. Ferrari and P. Vogel, SYNLETT, 1991, 233.

Monofunctional ether initiators (I) are prepared in accord with the process of this invention and such compounds can include, but are not limited to, 3-(1,1-dimethylethoxy)-1-propyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 4-(ethoxy)-1-butyllithium, 4-(1-propyloxy)-1-butyllithium, 4-(1-methylethoxy)-1-butyllithium, 3-(triphenylmethoxy)-2,2-dimethyl-1-propyllithium, 4-(triphenylmethoxy)-1-

- butyllithium, 5-(triphenylmethoxy)-1-pentyllithium, 6-(triphenylmethoxy)-1-hexyllithium, 8-(triphenylmethoxy)-1-octyllithium, 3-(1,1-dimethylpropyloxy)-1-propyllithium, 3-(1,1-dimethylpropyloxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropyloxy)-1-butyllithium,
- 5 3-[3-(dimethylamino)-1-propyloxy]-1-propyllithium, 3-[2-(dimethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diisopropyl)amino]-1-ethoxy]-1-propyllithium, 3-[2-(1-piperidino)-1-ethoxy]-1-propyllithium, 3-[2-(1-pyrrolidino)-1-ethoxy]-1-propyllithium, 4-[3-(dimethylamino)-1-propyloxy]-1-butyllithium, 6-[2-(1-piperidino)-1-ethoxy]-1-
- 10 hexyllithium, 3-[2-(methoxy)-1-ethoxy]-1-propyllithium, 3-[2-(ethoxy)-1-ethoxy]-1-propyllithium, 4-[2-(methoxy)-1-ethoxy]-1-butyllithium, 5-[2-(ethoxy)-1-ethoxy]-1-pentyllithium, 3-[3-(methylthio)-1-propyloxy]-1-propyllithium, 3-[4-(methylthio)-1-butyloxy]-1-propyllithium, 3-(methylthiomethoxy)-1-propyllithium, 6-[3-(methylthio)-1-propyloxy]-1-
- 15 hexyllithium, 3-[4-(methoxy)-benzyloxy]-1-propyllithium, 3-[4-(1,1-dimethylethoxy)-benzyloxy]-1-propyllithium, 3-[2,4-(dimethoxy)-benzyloxy]-1-propyllithium, 8-[4-(methoxy)-benzyloxy]-1-octyllithium, 4-[4-(methylthio)-benzyloxy]-1-butyllithium, 3-[4-(dimethylamino)-benzyloxy]-1-propyllithium, 6-[4-(dimethylamino)-benzyloxy]-1-hexyllithium,
- 20 6-(1,1-dimethylpropyloxy)-1-hexyllithium, 4-methoxy-1-butyllithium, 3-methoxy-1-butyllithium, 3-(triphenylmethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, and 3-(1,1-dimethylpropyloxy)-2-methyl-1-propyllithium.

- Lithium metal used in preparing the monofunctional ether initiators
- 25 (I) is used as a dispersion whose particle size usually does not exceed about 300 microns. Preferably the particle size is between 10 and 300 microns although coarser particle size lithium can be used. The lithium metal can contain 0.2 to 0.8 and preferably 0.3 to 0.5 weight percent sodium. The lithium metal is used in amounts of 90% of theoretical to a
- 30 40% excess above the theoretical amount necessary to produce the monofunctional ether initiators (I).

The preferred reaction temperatures vary from compound to compound, with each compound tending to have its own preferred reaction conditions. Surprisingly, for some compounds the preferred

reaction temperature/condition is the reflux temperature of the solvent. When this is the case the preferred reaction temperature is in the range of 35 to 80° C.

Solvents useful in practicing this invention include but are not limited to inert liquid alkanes, cycloalkanes and aryl solvents such as alkanes and cycloalkanes containing five to 10 carbon atoms such as pentane, hexane, cyclohexane, methylcyclohexane, heptane, methylcycloheptane, octane, decane and so forth and aryl solvents containing six to ten carbon atoms such as toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, n-propylbenzene, isopropylbenzene, n-butylbenzene, and the like.

Advantages of using the compounds containing the protecting groups of this invention comprising the process of producing a lithium initiator and subsequently in using the said initiator to produce polymers containing the said protecting groups as compared to using substituted silyl protecting groups are as follows: 1) cheaper and more readily available raw materials are used in the preparation of initiators, e.g. inexpensive olefins such as isobutylene or isoamylene are reacted with omega halo-alcohol as compared to the use of the more expensive alkyl chlorosilanes, such as tert-butyldimethylchlorosilane or diphenylmethylchlorosilane. 2) The excellent stability of the protective group to most reagents except strong acids [comparable to tert-butyldimethylsilyl group] 3) The protecting groups of this invention can be removed in as many ways and as simply as any of the substituted silyl protecting groups. Thus, for example, a tert-butyl protecting group on a hydroxy terminated polymer can be removed with a) anhydrous triflic acid b) HBr in acetic acid c) HCl in dioxane d) acetic anhydride in ethyl ether (FeCl₃ catalyst) e) TiCl₄ in CH₂Cl₂ (T.W. Greene, Protective Groups in Organic Chemistry, Wiley, New York, 1981, pp 41-42) f) catalytic amounts of tert-butyldimethylsilyl triflate in methylene chloride (X. Frank et al , Tetrahedron Letters, 36, (5), 711 (1995). g) Amberlyst acidic ion exchange resin may also be employed at elevated temperatures. 4) The by-products of the deprotection step are easy to remove from the polymer. For example, the by-product of the deprotection reaction of the tert-butyl

protected hydroxypolymer is isobutylene, which is innocuous and does not require removal from the polymer, although it can be removed easily at temperatures above 100 degrees C during deprotection (see US 4,886, 446). The by-product of the deprotection of an alkylsilyl protected hydroxy
 5 polymer is an alkylsiloxane which is a contaminant that may require removal from the polymer.

Anionic polymerizations employing the herein described monofunctional ether initiators of this invention are conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal
 10 modifier, using an olefinic monomer which is an alkene or a 1,3-diene at a temperature of about -30° C to about +100° C. The polymerization reaction proceeds from initiation to propagation and finally termination so that the polymer is mono-functional or dysfunctional terminated. The polymers have molecular weight ranges of about 1000 to 10,000.
 15 Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

The present invention also provides a process for the anionic polymerization of anionically polymerizable monomers comprising the steps of:

a) initiating polymerization of a conjugated diene hydrocarbon
 20 monomer or an alkenylsubstituted aromatic hydrocarbon monomer in a hydrocarbon or mixed hydrocarbon-polar solvent medium at a temperature of 10 °C to 70° C with an initiator having the formula:



wherein M is an alkali metal, preferably lithium, Z is a branched or straight
 25 chain hydrocarbon tether or connecting group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; and R¹, R², and R³ are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkoxy, lower
 30 alkylthio, and lower dialkylamino groups to produce an intermediate polymer of formula Li-(Q)_m-Z-OC(R¹R²R³) wherein Q is a unit of polymerized conjugated diene or alkenylsubstituted aromatic hydrocarbon and Z, R¹R² and R³ have the meanings ascribed above, m is the number of units of the polymerized conjugated diene or alkenylsubstituted
 35 aromatic hydrocarbon and may vary from 10 to 200 units: reacting the

intermediate polymer with a compound selected from ethylene oxide, oxygen, carbon dioxide, sulfur, omega-alkenylarylhalosilanes (as exemplified by styrenyldimethylchlorosilane), isomeric divinylbenzenes, chlorosilanes (as exemplified by silicon tetrachloride and dimethyldichlorosilane, and chlorostannanes (as exemplified by tin tetrachloride and dibutyltin dichloride) and other materials known in the art to be useful for terminating, end capping or coupling of polymers; optionally hydrogenating the polymer; and

5 b) recovering a linear or branched polymer having one or more terminal functional groups, having the formula $FG-(Q)_m-Z-OC(R_1R_2R_3)$ wherein FG is a functional group derived by reaction of the intermediate polymer with one of the selected functionalizing compounds described above and m is the number of units of the polymerized conjugated diene or alkenylsubstituted aromatic hydrocarbon and may vary from 10 to 200

15 c) further reacting the functional polymer with other comonomers such as diesters, diisocyanates, di- or cyclic amides, and diols in the presence of a strong acid catalyst to simultaneously deprotect the functional polymer and polymerize both functional ends thereof to produce novel segmented block polymers, or

20 d) further reacting the functional polymer with other comonomers in the absence of a strong acid catalyst to yield novel block polymers, while maintaining the integrity of the protective group, or

e) further removing the protective group from the resultant polymer from d) above followed by reaction with the same or other comonomers to produce novel segmented block polymers.

25 The olefinic monomer to be anionically polymerized by the monofunctional ether initiator is preferably a conjugated diene or an alkenylaromatic hydrocarbon. The conjugated diene or alkenylaromatic compound will be chosen from the group of unsaturated organic compounds that can be polymerized anionically (i.e., in a reaction initiated by an organo- alkali metal). Suitable alkenylaromatics include the optionally-substituted styrenes and vinylnaphthalenes. Alkenylsubstituted aromatic hydrocarbons useful in practicing this invention include but are not limited to styrene, alpha-methylstyrene, vinyltoluene, 1-vinylnaphthalene, 3-methylstyrene, 4-methylstyrene, 1,1-diphenylethylene

and the like. Suitable 1,3-dienes will preferably contain from 4 to 12, especially from 4 to 8, carbon atoms per molecule. Examples of these compounds include, but are not limited to, the following : 1,3-butadiene, isoprene; 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-3-ethyl-
 5 1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene; 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, and 2-methyl-3-isopropyl-1,3-butadiene.

10 Among the dialkylbutadienes, it is preferred that the alkyl groups contain from 1 to 3 carbon atoms. Of the above monomers 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene are preferred with 1,3-butadiene being particularly preferred. The dienes may be polymerised alone, or in admixture with each other or with alkenylaromatic
 15 compounds to form random copolymers, or by charging the dienes to the reaction mixture sequentially, either with each other or with alkenylaromatic compounds, to form block copolymers.

For example, a protected functional living polymer of this invention can be generated by polymerizing 1,3-butadiene with an initiator of
 20 formula I above, wherein M is lithium, Z is a trimethylene tether or connecting group, and R¹, R², and R³ are methyl groups. A living polymer is produced having the formula



where B is a unit derived by polymerizing butadiene, and m is an integer
 25 from about 10 to 200. The living polymer III, may be reacted, for example, with ethylene oxide to yield, after hydrolysis, the compound of formula



which may optionally be hydrogenated to the corresponding asymmetric polymer.

30 Additionally, other asymmetrically difunctional polymers may be produced by reacting the living polymer (III) above with, for example, carbon dioxide to produce, a polymer with one protected hydroxyl and one carboxyl group, or the living polymer III may be reacted with 1,5 diazabicyclo-(3.1.0) hexane as described in US 4,753,991 to produce a
 35 polymer with one protected hydroxyl and one amino group.

Other asymmetrically substituted monofunctional polymers may be produced having epoxy or isocyanate groups at one end for example by reacting the lithium salt of IV above (before hydrolysis), with epichlorohydrin or, by reacting IV itself with an equivalent of a diisocyanate, such as methylene 4,4-diphenyl diisocyanate (2/1 NCO/OH). These unsymmetrically substituted difunctional polymers could then be further reacted with other comonomers either with or without simultaneous deprotection as described above.

The protected monohydroxy polymers (IV) alone and in their hydrogenated forms, could be used as base materials to lend flexibility and higher impact strength in a number of formulas to produce coatings, sealants, binders and block copolymers with polyesters, polyamides and polycarbonates as described in UK Patent Application GB2270317A and in "Polytail" data sheets and brochures (Mitsubishi Kasei America).

Thus, in the presence of acidic catalysts used to promote the formation of many of these block copolymer resins, the protective group of the hydrogenated polymer is removed as well, allowing the exposed hydroxyl grouping in the base polymer molecule to simultaneously participate in the block copolymer reaction.

Thus, for example, hydrogenated IV polymers may be reacted with bisphenol A and phosgene in the presence of appropriate catalysts with simultaneous deprotection to yield a polycarbonate alternating block copolymer. The resulting products are useful as molding resins, for example, to prepare interior components for automobiles.

A segmented polyamide-hydrogenated IV block copolymer also useful as a molding composition to prepare exterior automotive components can be prepared by reacting hydrogenated IV polymer with caprolactam and adipic acid in the presence of a suitable catalyst.

A segmented polyester-hydrogenated IV block copolymer can be produced by reaction of hydrogenated IV polymer with dimethyl terephthalate and a suitable acidic catalyst. Again, the products are useful as molding compounds for exterior automotive components.

Isocyanate-terminated prepolymers can be produced from hydrogenated IV polymers by reaction with suitable diisocyanates (2/1 NCO/OH) as above which can be further reacted with diols and additional

diisocyanates to form segmented polyurethanes useful for water based, low VOC coatings. Or segmented polyurethane prepolymers may be mixed with tackifying resins and used as a moisture-curable sealant, caulk or coating.

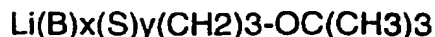
- 5 An acrylate-terminated prepolymer curable by free-radical processes can be prepared from the hydrogenated IV polymer by reaction with a diisocyanate (2NCO/OH) followed by further reaction with hydroxyethyl acrylate in the presence of a basic reagent.

- 10 Alternatively, the protected monohydroxy terminated polymer (IV) may be reacted with functional comonomers, without simultaneously removing the protective group, to produce novel copolymers. These copolymers may be deprotected and then further reacted with the same or different comonomers to form yet other novel copolymers. Thus, for example, the hydroxyterminated polymer of formula (IV) may be
15 hydrogenated, and then reacted with ethylene oxide in the presence of potassium tert-butoxide to produce a poly(ethyleneoxide)-hydrogenated polybutadiene copolymer with one protected hydroxyl group on the polybutadiene segment. This hydroxyl can then be deprotected and a poly(ethyleneoxide) polymer having different chain lengths grown onto
20 both ends of the polybutadiene segment.

- These processes can be applied to the deprotected and optionally hydrogenated polymers of formula IV, as well. Thus, alternatively, the protective group could be removed first from the hydrogenated polymer, and then the block copolymers formed by addition of the appropriate
25 comonomers .

- In another possible application, the living polymer III may be reacted with an alkenylarylhalosilane such as styrenyldimethylchlorosilane to yield the corresponding omega-styrenylterminated macromonomer according to directions in US5,278,244 which may be further polymerized
30 by a variety of techniques to yield "comb" polymers which, on deprotection and hydrogenation yield branched polymers with hydroxyfunctionality on the branch-ends. Such multi-functionality can be utilized to graft a water-soluble polymer such as polyethylene oxide onto a hydrophobic polyolefinic core to produce hydrogels.

In still another example, a living polymer analogous to III having the formula



where B is polymerized butadiene, S is polymerized styrene and x and y
5 can vary from 10 to 1000 or more is reacted with divinylbenzene (DVB) to produce a multi-armed star polymer, according to US4,409,357 which on hydrogenation and deprotection would yield a star with hydroxy-functional branches which may be further reacted with ethylene oxide and potassium alkoxide as described above to produce hydrogels.

10 In still another possible application, the hydrogenated hydroxyterminated branches of the star polymer may be further reacted with acryloyl chloride or methacryloyl chloride, and the resultant acrylate or methacrylate-terminated polymer further polymerized with monomers
15 selected from the group of alkyl acrylates, alkyl methacrylates, and dialkylacrylamides to produce hydrogels. Star polymers are useful as viscosity index improver for motor oils.

Other monomers may be reacted directly with formula III type compounds to yield block or star copolymers.

The following examples further illustrate the invention.

20

EXAMPLE 1

PREPARATION OF 3-(1,1-DIMETHYLETHOXY)-1-PROPYLLITHIUM IN CYCLOHEXANE, LOT 8888

25

A 500 ml., three-necked, Morton flask was fitted with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot,
30 and allowed to cool to room temperature in a stream of argon. Lithium metal dispersion, lot 8200, 0.61% sodium, was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml). The resultant lithium dispersion was dried in a stream of argon, weighed (4.07 grams, 0.586 mole, 2.80 equivalents), and transferred to the reaction flask with 150 ml
35 of cyclohexane. The reaction mixture was stirred at 450 RPMs, and

- heated to 70° C with a heating mantle. The heat source was removed. 1-Chloro-3-(1,1-dimethylethoxy)-propane, 31.52 grams, (0.209 mole, 1.00 equivalent, lot 8864) was added dropwise via the addition funnel. An exotherm was detected after 5.5% of the halide feed had been added. A
- 5 dry ice/hexane cooling bath was applied as needed to maintain the reaction temperature between 60-65° C. The total halide feed time was fifty-two minutes. The cooling bath was removed at the end of the halide feed. The reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for one hour at 450 RPMs, and two and one
- 10 half hours at 300 RPMs. The reaction mixture was transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure filtered with 3 psi (20.68×10^3 Pa) argon. The lithium chloride muds were reslurried with fresh cyclohexane (2 X 50 ml.). The filtrate was a clear, yellow solution, yield = 230 ml., 185.03 grams.
- 15 Total Base = 3.85 wt. %.
Active C-Li = 3.78 wt. %.
Yield = 27.4 % (based on active analysis).

- A one ml. aliquot of this solution was carefully quenched with water.
- 20 The organic phase was analyzed by Gas Chromatography (30 m. X 0.54 mm AT-1 column). 1-Chloro-3-(1,1-dimethylethoxy)-propane (retention time = 13.58 minutes) was not detected. The corresponding des-chloro material (retention time = 8.36 minutes) was identified by GC/MS.
- 25 The very thick lithium chloride mud cake was washed with dry dibutylether (3 X 50 ml.). This afforded a clear, colorless solution, yield = 200ml., 154.76 grams.
- Total Base = 5.69 wt %.
Active C-Li = 3.32 wt. %.
- 30 Yield = 20.1 % (based on active analysis).

The total yield was 47.6 %.

PREPARATION OF 3-(1,1-DIMETHYLETHOXY)-2,2-DIMETHYL-1-
PROPYLLITHIUM IN CYCLOHEXANE, LOT 8923

- A 500 ml., three-necked, Morton flask was fitted with a mechanical stirrer,
5 a 125 ml pressure-equalizing addition funnel, and a Claisen adapter
equipped with a thermocouple, a dry ice condenser, and an argon inlet.
This apparatus was dried in an oven overnight at 125° C, assembled hot,
and allowed to cool to room temperature in a stream of argon. Lithium
metal dispersion, lot 8200, 0.61% sodium, was washed free of mineral oil
10 with hexane (2 X 70 ml), and pentane (1 X 70 ml). The resultant lithium
dispersion was dried in a stream of argon, weighed (4.40 grams, 0.634
mole, 2.80 equivalents), and transferred to the reaction flask with 200 ml
of cyclohexane. The reaction mixture was stirred at 450 RPMs, and
heated to 65° C with a heating mantle. The heat source was removed. 1-
15 Chloro-3-(1,1-dimethylethoxy)-2,2-dimethyl-propane, 40.42 grams, (0.226
mole, 1.00 equivalent, lot 8913) was added dropwise via the addition
funnel. An exotherm was detected after 12.8% of the halide feed had
been added. A dry ice/hexane cooling bath was applied as needed to
maintain the reaction temperature between 60-65° C. The total halide
20 feed time was one hour. The cooling bath was removed at the end of the
halide feed. The reaction temperature fell off rapidly to room temperature.
The reaction mixture was stirred for eighty minutes at 450 RPMs. The
reaction mixture was then transferred with argon pressure to a dry sintered
glass pressure filter. The product solution was pressure filtered with 3 psi
25 (20.68 x 10³ Pa) argon. The lithium chloride muds were reslurried with
fresh cyclohexane (2 X 40 ml.). The filtrate was a clear, pale yellow
solution, yield = 320 ml., 251.91 grams. A white solid precipitated from
solution immediately after the filtration.
Analysis of the supernatant solution:
30 Total Base = 7.4 wt. %.
Active C-Li = 7.0 wt. %.
Yield = 52.0% (based on active analysis).
Analysis of the slurry:
Total Base = 12.4 wt. %.
35 Active C-Li = 11.9 wt. %.

Yield = 88.4% (based on active analysis).

EXAMPLE 3

5 PREPARATION OF 3-(1,1-DIMETHYLPROPYLOXY)-1-PROPYLLITHIUM IN CYCLOHEXANE, LOT 9135

A one liter, three-necked, Morton flask was fitted with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter
10 equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium metal dispersion, lot 8899, 0.43% sodium, was washed free of mineral oil with hexane (2 X 100 ml), and pentane (1 X 100 ml). The resultant lithium
15 dispersion was dried in a stream of argon, weighed (6.35 grams, 0.915 mole, 3.67 equivalents), and transferred to the reaction flask with 180 ml of cyclohexane. The reaction mixture was stirred at 450 RPMs, and heated to 65° C with a heating mantle. The heat source was removed. 1-Chloro-3-(1,1-dimethylpropyloxy)-propane, 41.00 grams, (0.249 mole, 1.00
20 equivalent, lot 9118, 9134) was added dropwise via the addition funnel. An exotherm was detected after 13% of the feed had been added. A dry ice/hexane cooling bath was applied as needed to maintain the reaction temperature between 60-65° C. The total halide feed time was sixty-five minutes. The cooling bath was removed at the end of the halide feed.
25 The reaction temperature fell off gradually to room temperature. The reaction mixture was stirred for one hour at 450 RPMs, and one hour at 300 RPMs. The reaction mixture was transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure filtered with 3 psi (20.68×10^3 Pa) argon. The lithium chloride muds were
30 reslurried with fresh cyclohexane (2 X 50 ml.). The filtrate was a clear, pale yellow solution, yield = 250 ml., 190.86 grams.
Total Base = 6.32 wt. %.
Active C-Li = 5.01 wt. %.
Yield = 28.2% (based on active analysis).

EXAMPLE 4

PREPARATION OF 3-(1,1-DIMETHYLPROPYLOXY)-2,2-DIMETHYL-1-
PROPYLLITHIUM IN CYCLOHEXANE, LOT 9167

5 A one liter, three-necked, Morton flask was fitted with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot,
10 and allowed to cool to room temperature in a stream of argon. Lithium metal dispersion, lot 8899, 0.43% sodium, was washed free of mineral oil with hexane (2 X 100 ml), and pentane (1 X 100 ml). The resultant lithium dispersion was dried in a stream of argon, weighed (3.33 grams, 0.480 mole, 2.86 equivalents), and transferred to the reaction flask with 150 ml
15 of cyclohexane. The reaction mixture was stirred at 450 RPMs, and heated to 65° C with a heating mantle. The heat source was removed. 1-Chloro-3-(1,1-dimethylpropyloxy)-2,2-dimethyl-propane, 33.00 grams, (0.168 mole, 1.00 equivalent, lot 9152) was added dropwise via the addition funnel. An exotherm was detected after 22% of the halide feed
20 had been added. A dry ice/hexane cooling bath was applied as needed to maintain the reaction temperature between 60-65° C. The total halide feed time was fifty-three minutes. The cooling bath was removed at the end of the halide feed. The reaction temperature fell off gradually to room temperature. The reaction mixture was stirred for forty-five minutes at 450
25 RPMs, and seventy-five minutes at 300 RPMs. The reaction mixture was transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure filtered with 3 psi (20.68×10^3 Pa) argon. The lithium chloride muds were reslurried with fresh cyclohexane (2 X 50 ml.). The filtrate was a clear, pale yellow solution, yield = 250 ml., 194.93
30 grams.
Total Base = 12.4 wt. %.
Active C-Li = 11.3 wt. %.
Yield = 78.3 % (based on active analysis).

EXAMPLE 5
PREPARATION OF 4-METHOXY-1-BUTYLLITHIUM IN CYCLOHEXANE
LOT 8916

- 5 A 500 ml., three-necked, Morton flask was fitted with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium
- 10 metal dispersion, lot 8200, 0.61% sodium, was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml). The resultant lithium dispersion was dried in a stream of argon, weighed (7.25 grams, 1.045 mole, 2.80 equivalents), and transferred to the reaction flask with 200 ml of cyclohexane. The reaction mixture was stirred at 450 RPMs, and
- 15 heated to 72.6° C with a heating mantle. The heat source was removed. 1-Chloro-4-methoxy-butane, 45.70 grams, (0.373 mole, 1.00 equivalent, lot 8663) was added dropwise via the addition funnel. An exotherm was detected after 7.8% of the feed had been added. Hexane/dry ice cooling was applied to maintain the reaction temperature at 60-65° C. The total
- 20 halide feed time was sixty-five minutes. The cooling bath was removed at the end of the halide feed. The reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for one hour at 450 RPMs. The reaction mixture was then transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure
- 25 filtered with 5 psi (20.68×10^3 Pa) argon. The lithium chloride muds were reslurried with fresh cyclohexane (2 X 40 ml.). The filtrate was a clear, very pale yellow solution, yield = 300 ml., 242.28 grams.
- Total Base = 12.4 wt. %.
- Active C-Li = 12.1 wt. %.
- 30 Yield = 83.6% (based on active analysis).

EXAMPLE 6
PREPARATION OF 3-METHOXY-1-BUTYLLITHIUM IN CYCLOHEXANE,
LOT 8939

35

A 500 ml., three-necked, Morton flask was fitted with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium metal dispersion, lot 8899, 0.43% sodium, was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml). The resultant lithium dispersion was dried in a stream of argon, weighed (6.35 grams, 0.915 mole, 2.80 equivalents), and transferred to the reaction flask with 200 ml of cyclohexane. The reaction mixture was stirred at 450 RPMs, and heated to 68° C with a heating mantle. The heat source was removed. 1-Chloro-3-methoxy-butane, 40.03 grams, (0.327 mole, 1.00 equivalent, lot 8914) was added dropwise via the addition funnel. An exotherm was detected after 7.5% of the feed had been added. A dry ice/hexane cooling bath was applied as needed to maintain the reaction temperature between 60-65° C. The total halide feed time was eighty-three minutes. The cooling bath was removed at the end of the halide feed. The reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for one hour at 450 RPMs. The reaction mixture was then transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure filtered with 3 psi (20.68 x 10³ Pa) argon. The lithium chloride muds were reslurried with fresh cyclohexane (2 X 75 ml.). The filtrate was a clear, pale yellow solution, yield = 280 ml., 215.70 grams.

Total Base = 13.58 wt. %.

Active C-Li = 13.12 wt. %.

Yield = 92.1 % (based on active analysis).

Soluble chloride = 62 ppm.

30

EXAMPLE 7
PREPARATION OF 4-(2-BUTOXY)-1-BUTYLLITHIUM IN
CYCLOHEXANE, LOT 8956

35

A 500 ml., three-necked, Morton flask was fitted with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled
5 hot, and allowed to cool to room temperature in a stream of argon. Lithium metal dispersion, lot 8899, 0.43% sodium, was washed free of mineral oil with hexane (2 X 100 ml), and pentane (1 X 100 ml). The resultant lithium dispersion was dried in a stream of argon, weighed (6.70
10 grams, 0.965 mole, 2.80 equivalents), and transferred to the reaction flask with 250 ml of cyclohexane. The reaction mixture was stirred at 450 RPMs, and heated to 65° C with a heating mantle. The heat source was removed. 4-(2-Butoxy)-1-chloro-butane, 56.72 grams, (0.345 mole, 1.00 equivalent, lot 8921) was added dropwise via the addition funnel. An exotherm was detected after 15.6% of the halide feed had been added. A
15 dry ice/hexane cooling bath was applied as needed to maintain the reaction temperature between 60-65° C. The total halide feed time was seventy-two minutes. The cooling bath was removed at the end of the halide feed. The reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for one hour at 450 RPMs. The reaction
20 mixture was then transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure filtered with 3 psi (20.68 x 10³ Pa) argon. The lithium chloride muds were reslurried with fresh cyclohexane (1 X 75 ml., 1 X 50 ml.). The filtrate was a clear, yellow solution, yield = 440 ml., 348.84 grams.
25 Total Base = 12.1 wt. %.
Active C-Li = 11.2 wt. %.
Yield = 83.3 % (based on active analysis).

30

EXAMPLE 8

PREPARATION OF 4-(1-METHYLETHOXY)-1-BUTYLLITHIUM IN CYCLOHEXANE, LOT 9042

A 500 ml., three-necked, Morton flask was fitted with a mechanical stirrer,
35 a 125 ml pressure-equalizing addition funnel, and a Claisen adapter

equipped with a thermocouple, a dry ice condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium metal dispersion, lot 8899, 0.43% sodium, was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml). The resultant lithium dispersion was dried in a stream of argon, weighed (6.00 grams, 0.864 mole, 2.80 equivalents), and transferred to the reaction flask with 250 ml of cyclohexane. The reaction mixture was stirred at 450 RPMs, and heated to 80° C with a heating mantle. The heat source was removed. 1-Chloro-4-(1-methylethoxy)-butane, 46.47 grams, (0.309 mole, 1.00 equivalent, lot 8960) was added dropwise via the addition funnel. An exotherm was detected after 22.9 % of the halide feed had been added. A dry ice/hexane cooling bath was applied as needed to maintain the reaction temperature between 60-65° C. The total halide feed time was forty-five minutes. The cooling bath was removed at the end of the halide feed. The reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for ninety minutes at 450 RPMs, then for two hours at 300 RPMs. The reaction mixture was then transferred with argon pressure to a dry sintered glass pressure filter. The product solution was pressure filtered with 3 psi (20.68×10^3 Pa) argon. The lithium chloride muds were reslurried with fresh cyclohexane (2 X 25 ml.). The filtrate was a clear, yellow solution, yield = 350 ml., 264.91 grams.

Total Base = 12.3 wt. %.

Active C-Li = 11.0 wt. %.

Yield = 77.3 % (based on active analysis).

POLYMERIZATION EXAMPLE

POLYMERIZATION OF ISOPRENE WITH 4-METHOXY-1-BUTYLLITHIUM, LOT 8970

A one liter, three-necked, round-bottom flask was fitted with a mechanical stirrer, a septum and a Claisen adapter equipped with a thermocouple, dry ice condenser, and an argon inlet. This apparatus was dried in an oven

overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with cyclohexane, 310.70 grams, and isoprene, 40.00 grams (0.587 mole). The reaction mixture was at 20.0° C. 4-Methoxy-1-butyllithium, 16.74
5 grams of 11.4 wt.% solution (0.020 mole, Lot 8915) was then added with a syringe. An exotherm of 1°C was detected. The clear solution was heated to 48.4° C with a heating mantle. The heat source was removed. The reaction temperature proceeded to climb steadily to 53.4° C, at which time a dry ice/hexane cooling bath was employed for a few minutes to
10 moderate the temperature. The cooling bath was then removed. The reaction temperature gradually declined to 24.2° C in one hour. The reaction mixture was stirred at room temperature for sixteen hours, then quenched with methanol (40 ml.) and hexane (100 ml.). The reaction mixture was transferred to a one liter separatory funnel, and the methanol
15 layer was discarded. The hydrocarbon layer was washed with an additional 40 ml. of methanol, and concentrated to constant weight on the rotary evaporator, at a bath temperature of 35° C. This afforded a clear, somewhat viscous oil, yield = 39.00 grams (97.3%).
VPO analysis, Mn = 1996.
20 GPC analysis, MWD = 1.48.

The remaining polymerization data is collected in the Table.

25

PREPARATION OF STARTING MATERIALS

1. 1-CHLORO-3-(1,1-DIMETHYLETHOXY)-PROPANE, LOT 8864

A two liter, three-necked round bottom flask was fitted with a mechanical
30 stirrer, a gas inlet tube, and a Claisen adapter equipped with a dry ice condenser, and a thermocouple. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with 141.81 grams (1.50 moles, 1.00 equivalent) of 3-chloro-1-propanol and 500 ml. of
35 cyclohexane. The resultant two-phase solution was stirred at 400 RPMs.

- Amberlyst 15 resin catalyst, 35 grams, was added, followed by an additional 250 ml. of cyclohexane. A total of 93 grams (1.657 moles, 1.105 equivalents) of 2-methylpropene was discharged from the cylinder in two and a third hours. A modest exotherm was noted during the addition.
- 5 The reaction mixture was stirred at 20-25° C, and periodically monitored by gas chromatography (GC) for the disappearance of 3-chloro-1-propanol. After stirring at room temperature for twenty-eight hours, the conversion to the desired product was 94.7 %. The catalyst was removed by filtration through a piece of fluted filter paper. The reaction flask was
- 10 rinsed with fresh cyclohexane (2 X 100 ml.). The product was purified by distillation from 10.72 grams of potassium carbonate through a twelve inch Vigreux column, at atmospheric pressure. This afforded a clear, colorless oil, yield = 158.42 grams (70.2 %).
B.P. = 151.0 - 154.8° C.
- 15 GC assay = 0.59 % 2-methylpropene, 2.54 % cyclohexane, 87.15 % desired product, and 9.72 % unknowns.
NMR (CDCl₃): 3.63 (t, J = 6 Hz, 2H), 3.46 (t, J = 6 Hz, 2H), 2.28 - 1.62 (m, 2H), 1.21 (s, 9H) ppm.

20

2. 1-CHLORO-3-(1,1-DIMETHYLETHOXY)-2,2-DIMETHYL-PROPANE, LOT 8913

- A one liter, three-necked round bottom flask was fitted with a
- 25 mechanical stirrer, a gas inlet tube, and a Claisen adapter equipped with a dry ice condenser, and a thermocouple. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with 91.95 grams (0.75 moles, 1.00 equivalent) of 3-chloro-2,2-dimethyl-1-propanol
- 30 and 200 ml. of cyclohexane. The resultant one-phase solution was stirred at 400 RPMs. Amberlyst 15 resin catalyst, 15 grams, was added, followed by an additional 50 ml. of cyclohexane. A total of 48.4 grams (0.86 moles, 1.15 equivalents) of 2-methylpropene was discharged from the cylinder in three and a half hours. A modest exotherm was noted during the addition.
- 35 The reaction mixture was stirred at 20-25° C, and periodically monitored

by gas chromatography (GC) for the disappearance of 3-chloro-2,2-dimethyl-1-propanol. After stirring at room temperature for twenty hours, all the starting material had been consumed, with the formation of a single, higher-boiling compound. The catalyst was removed by filtration through a
5 piece of fluted filter paper. The reaction flask was rinsed with fresh cyclohexane (2 X 50 ml.). The product was purified by distillation from 5.07 grams of potassium carbonate through a twelve inch Vigreux column, at atmospheric pressure. This afforded a clear, colorless oil, yield = 111.21 grams (83.0 %).
10 B.P. = 169.0 - 174.0°C.
GC assay = 2.98 % cyclohexane, 16.79 % 3-chloro-2,2-dimethyl-1-propanol, 78.06 % desired product, and 1.17 % unknowns.

15 3. 1-CHLORO-3-(1,1-DIMETHYLPROPYLOXY)-PROPANE, LOT 9245

A 500 ml., three-necked round bottom flask was fitted with a reflux condenser, a thermocouple, a septum inlet, a magnetic stir bar, and an
20 argon inlet. The flask was charged with 3-chloro-1-propanol, 94.54 grams (1.00 mole, 1.00 equivalents), pentane (50 ml.), and 2-methyl-2-butene, 70.44 grams (1.00 mole, 1.00 equivalents). This afforded a two phase solution. The reaction mixture was maintained at 20-25° C with a water cooling bath. Boron trifluoride etherate, 13.85 grams (0.098 mole, 0.098
25 equivalents) was added rapidly via syringe. A mild exotherm, 4-5° C, ensued, which subsided in fifteen minutes. The reaction mixture was stirred at 20-25° C, and periodically monitored by gas chromatography (GC) for the disappearance of 3-chloro-1-propanol. After forty-eight hours
30 stirring, all the starting material had been consumed, and the reaction mixture was a single phase. The reaction mixture was diluted with pentane (100 ml.) and water (100 ml.) and transferred to a separatory funnel. The aqueous layer was discarded. The organic layer was washed with saturated sodium bicarbonate solution (2 X 50 ml.), water (1 X 50 ml.), and filter-dried over magnesium sulfate. The filtrate was

concentrated on the rotary evaporator at room temperature to afford a pale yellow liquid, yield = 113.47 grams (69.0%).

GC assay = 96.7 % desired product, 3.3 % unknowns.

NMR (CDCl₃): 3.65 (t, J = 6 Hz, 2H), 3.45 (t, J = 6 Hz, 2H), 2.00 (q, J = 6 Hz, 2 H), 1.80-1.25 (m, 2H), 1.13 (s, 6H), and 0.84 (t, J = 6 Hz, 3H) ppm.

4. 1-CHLORO-3-(1,1-DIMETHYLPROPYLOXY)-2,2-DIMETHYL-PROPANE, LOT 9250

10

A 500 ml., three-necked round bottom flask was fitted with a reflux condenser, a thermocouple, a septum inlet, a magnetic stir bar, and an argon inlet. The flask was charged with 3-chloro-2,2-dimethyl-1-propanol, 122.60 grams (1.00 mole, 1.00 equivalents), pentane (50 ml.), and 2-methyl-2-butene, 70.66 grams (1.01 mole, 1.01 equivalents). This afforded a two phase solution. The reaction mixture was maintained at 20-25° C with a water cooling bath. Boron trifluoride etherate, 13.85 grams (0.098 mole, 0.098 equivalents) was added rapidly via syringe. A mild exotherm, 4-5° C, ensued, which subsided in fifteen minutes. The reaction mixture was stirred at 20-25°C, and periodically monitored by gas chromatography (GC) for the disappearance of 3-chloro-2,2-dimethyl-1-propanol. After twenty-four hours stirring, all the starting material had been consumed, and the reaction mixture was a single phase. The reaction mixture was diluted with pentane (50 ml.) and water (100 ml.) and transferred to a separatory funnel. The aqueous layer was discarded. The organic layer was washed with saturated sodium bicarbonate solution (2 X 50 ml.), water (1 X 50 ml.), and filter-dried over magnesium sulfate. The filtrate was concentrated on the rotary evaporator at room temperature to afford a clear, almost colorless liquid, yield = 165.90 grams (86.1 %).

30

GC assay = 87.7 % desired product, 12.3 % unknowns.

NMR (CDCl₃): 3.45 (s, 2H), 3.09 (s, 2H), 1.81-1.20 (m, 2H), 1.09 (s, 6H), 0.95 (s, 6H), and 0.84 (t, J = 6 Hz, 3H).

35

5. 1-CHLORO-4-METHOXY-BUTANE, LOT 8663

A one liter, three-necked round bottom flask was equipped with a reflux condenser, a teflon clad thermocouple, a 225 ml. pressure-equalizing addition funnel, a large egg-shaped magnetic stir bar, and a gas outlet vented to a caustic scrubber. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with methanol, 80.10 grams (2.50 moles, 1.00 equivalent) and tetrahydrofuran, 180.28 grams (2.50 moles, 1.00 equivalent). The reaction mixture was cooled to 0° C with a methanol/ice bath, then 356.91 grams (3.00 moles, 1.20 equivalents) of thionyl chloride was added dropwise via the addition funnel. There was an immediate exotherm, and a release of acidic fumes. The temperature was held below 15° C by adjustment of the feed rate. The total thionyl chloride feed time was two and a third hours. The cooling bath was removed at the end of the feed. The reaction mixture was clear and colorless. The reaction mixture was heated to reflux for three hours, at which time the temperature was 120° C, then the reaction mixture was allowed to cool to room temperature. An aliquot was withdrawn, diluted with pentane, washed with water and saturated sodium bicarbonate solution, then analyzed by gas chromatography (30 m. X 0.54 mm AT-1 column). Both of the starting materials were still present, tetrahydrofuran (retention time = 3.46 minutes), methanol (retention time = 0.85 minutes), in addition to the desired product (retention time = 8.68 minutes). The reaction mixture was heated to reflux for an additional two hours, after which time all gas evolution had ceased. The reaction mixture was allowed to cool to room temperature, then the orange reaction mixture was transferred to a one liter separatory funnel, and diluted with pentane (300 ml.). The organic layer was washed with water (2 X 300 ml.), saturated sodium bicarbonate solution (1 X 300 ml.), and finally, water (2 X 300 ml.). The organic layer was dried (magnesium sulfate), filtered, and purified by distillation through a six inch Vigreux column, at atmospheric pressure. This afforded a clear, colorless oil, yield = 187.63 grams (59.8 %). B.P. = 140.1-146.5°C.

GC assay = 0.28 % methanol, 0.17 % pentane, 0.64 % tetrahydrofuran, 97.68 % desired product, and 1.23 % unknowns.

NMR (D₆ Benzene): 3.43-2.89 (m, 4H), 3.12 (s, 3H), and 1.97-1.19 (m, 4H), ppm.

5

6. 1-CHLORO-3-METHOXY-BUTANE, LOT 8914

10 A 500 ml., three-necked round bottom flask was equipped with a reflux condenser, a teflon clad thermocouple, a 125 ml. pressure-equalizing addition funnel, a large egg-shaped magnetic stir bar, and a gas outlet vented to a caustic scrubber. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with thionyl chloride, 124.92 grams (1.05 moles, 1.05 equivalents). 3-Methoxy-1-butanol, 104.15 grams (1.00 mole, 1.00 equivalent) was added dropwise via the addition funnel. There was an immediate exotherm, and a release of acidic fumes. The total alcohol feed time was thirty-eight minutes. The reaction mixture was dark orange at the end of the feed. The reaction mixture was heated to reflux for four hours, then let cool to room temperature. An aliquot was withdrawn, diluted with pentane, washed with water and saturated sodium bicarbonate solution, then analyzed by gas chromatography (30 m. X 0.54 mm AT-1 column). All the starting material had been consumed, with the formation of a slightly faster eluting compound (3-methoxy-1-butanol retention time = 10.92 minutes, product retention time = 10.38 minutes). The reaction mixture was transferred to a one liter separatory funnel, diluted with pentane (300 ml.), and the organic layer was washed with water (2 X 300 ml.), saturated sodium bicarbonate solution (1 X 300 ml.), and finally, water (1 X 300 ml.). The organic layer was dried (magnesium sulfate), filtered, and distilled through a twelve inch Vigreux column, at atmospheric pressure. This afforded a clear, colorless oil, yield = 95.39 grams (77.9 %).

B.P. = 124.0 - 126.6°C.

GC assay = 1.6 % pentane, 94.2 % desired product, and 4.2 % unknowns.

NMR (CDCl₃): 3.99-3.43 (m, 3H), 3.35 (s, 3H), 2.13-1.59 (m, 2H), and 1.15 (t, J = 6 Hz, 3H) ppm.

5

7. 4-(2-BUTOXY)-1-CHLORO-BUTANE, LOT 8921

A one liter, three-necked round bottom flask was equipped with a reflux
10 condenser, a teflon clad thermocouple, a 250 ml. pressure-equalizing
addition funnel, a large egg-shaped magnetic stir bar, and a gas outlet
vented to a caustic scrubber. This apparatus was dried in an oven
overnight at 125° C, assembled hot, and allowed to cool to room
temperature in a stream of argon. The flask was charged with 2-butanol,
15 185.30 grams (2.50 moles, 1.00 equivalent) and tetrahydrofuran, 180.28
grams (2.50 moles, 1.00 equivalent). The reaction mixture was cooled to -
15°C, then 356.91 grams (3.00 moles, 1.20 equivalents) of thionyl
chloride was added dropwise via the addition funnel. There was an
immediate exotherm, and a release of acidic fumes. The temperature was
20 held below 10° C by adjustment of the feed rate. The total thionyl chloride
feed time was two and a quarter hours. The cooling bath was removed at
the end of the feed. The reaction mixture was heated to reflux (95° C) for
six hours, then let cool to room temperature. An aliquot was withdrawn,
diluted with pentane, washed with water and saturated sodium
25 bicarbonate solution, then analyzed by gas chromatography (30 m. X 0.54
mm AT-1 column). Both of the starting materials were still present,
tetrahydrofuran (retention time = 6.09 minutes), 2-butanol (retention time =
6.62 minutes), in addition to the desired product (retention time = 16.78
minutes). The reaction mixture was heated to reflux for an additional four
30 hours, after which time all gas evolution had ceased. The reaction mixture
was allowed to cool to room temperature, then transferred to a one liter
separatory funnel, and diluted with pentane (300 ml.). The organic layer
was washed with water (2 X 300 ml.), saturated sodium bicarbonate
solution (1 X 300 ml.), and finally, water (1 X 300 ml.). The organic layer
35 was dried (magnesium sulfate), filtered, and purified by distillation from

3.00 grams of potassium carbonate through a twelve inch Vigreux column, at atmospheric pressure. This afforded a clear, colorless oil, yield = 207.34 grams (50.4 %).

B.P. = 180.0 - 189.6° C.

5 GC assay = 96.0 % desired product, and 4.0 % unknowns.

NMR (CDCl₃): 3.72-2.91 (m, 5H), 2.03-1.12 (m, 6H), 0.99 (d, J = 6 Hz, 3H), and 0.74 (t, J = 6 Hz, 3H) ppm.

10 8. 1-CHLORO-4-(1-METHYLETHOXY)-BUTANE, LOT 8960

A one liter, three-necked round bottom flask was equipped with a reflux condenser, a teflon clad thermocouple, a 250 ml. pressure-equalizing addition funnel, a large egg-shaped magnetic stir bar, and a gas outlet
15 vented to a caustic scrubber. This apparatus was dried in an oven overnight at 125°C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with 2-propanol, 150.25 grams (2.50 moles, 1.00 equivalent) and tetrahydrofuran, 180.28 grams (2.50 moles, 1.00 equivalent). The reaction mixture was cooled to
20 0°C, then 356.91 grams (3.00 moles, 1.20 equivalents) of thionyl chloride was added dropwise via the addition funnel. There was an immediate exotherm, and a release of acidic fumes. The temperature was held below 15°C by adjustment of the feed rate. The total thionyl chloride feed time was two and a half hours. The cooling bath was removed at the end
25 of the feed. The reaction mixture was heated to reflux (119°C) for five hours, after which time all gas evolution had ceased, then let cool to room temperature. The orange reaction mixture was transferred to a one liter separatory funnel, and diluted with pentane (300 ml.). The organic layer was washed with water (2 X 400 ml.), saturated sodium bicarbonate
30 solution (1 X 300 ml.), and finally, water (1 X 300 ml.). The organic layer was dried (magnesium sulfate), filtered, and purified by distillation from 3.00 grams of potassium carbonate through a twelve inch Vigreux column, at atmospheric pressure. This afforded a clear, colorless oil, yield = 234.22 grams (61.8%). B.P. = 160.0 - 169.0°C
35 G.C. assay=88.0% desired products and 12.0% unknowns.

Claims:

1. A process for the preparation of hydrocarbon solutions of
5 monofunctional ether initiators characterized by reacting an omega-protected 1-haloalkyl containing 3 to 35 carbon atoms with a particulate alkali metal having particle sizes between 100 and 300 microns and selected from the group consisting of lithium, sodium and potassium, of the following structure:



- wherein M is an alkali metal selected from the group consisting of lithium, sodium and potassium; Z is defined as a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; R¹, R², and R³ are
15 independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkoxy, lower alkylthio and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkoxy, lower alkylthio or lower dialkylamino groups, comprising reacting an omega-protected-1-haloalkyl with an alkali metal having a particle size between
20 10 and 300 microns in size, at a temperature between 35 and 130° C in an alkane or cycloalkane solvent containing 5 to 10 carbon atoms to form an intermediate alkali metal-containing monofunctional ether product which product is reacted further with an unsaturated material selected from the group consisting of conjugated diene hydrocarbons and alkenyl
25 substituted aromatic hydrocarbons.

2. The process of claim 1 characterized in that the reaction temperature is the reflux temperature of the solvent.

3. The process of claim 1 characterized in that the omega-protected-1-haloalkane is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propylhalide, 3-(1,1-dimethylethoxy)-2-methyl-1-propylhalide, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propylhalide, 5-(1,1-
- 30

dimethylethoxy)-1-pentylhalide, 4-(1,1-dimethylethoxy)-1-butylhalide, 6-(1,1-dimethylethoxy)-1-hexylhalide, 8-(1,1-dimethylethoxy)-1-octylhalide, 4-(ethoxy)-1-butylhalide, 3-[3-(dimethylamino)-1-propyloxy]-1-propylhalide, 3-[2-(dimethylamino)-1-ethoxy]-1-propylhalide, 3-[2-(diethylamino)-1-ethoxy]-1-propylhalide, 3-[2-(diisopropyl)amino]-1-ethoxy]-1-propylhalide, 3-[2-(1-piperidino)-1-ethoxy]-1-propylhalide, 3-[2-(1-pyrrolidino)-1-ethoxy]-1-propylhalide, 4-[3-(dimethylamino)-1-propyloxy]-1-butylhalide, 6-[2-(1-piperidino)-1-ethoxy]-1-hexylhalide, 3-[2-(methoxy)-1-ethoxy]-1-propylhalide, 3-[2-(ethoxy)-1-ethoxy]-1-propylhalide, 4-[2-(methoxy)-1-ethoxy]-1-butylhalide, 5-[2-(ethoxy)-1-ethoxy]-1-pentylhalide, 3-[3-(methylthio)-1-propyloxy]-1-propylhalide, 3-[4-(methylthio)-1-butyloxy]-1-propylhalide, 3-(methylthiomethoxy)-1-propylhalide, 6-[3-(methylthio)-1-propyloxy]-1-hexylhalide, 3-[4-(methoxy)-benzyloxy]-1-propylhalide, 3-[4-(1,1-dimethylethoxy)-benzyloxy]-1-propylhalide, 3-[2,4-(dimethoxy)-benzyloxy]-1-propylhalide, 8-[4-(methoxy)-benzyloxy]-1-octylhalide, 4-[4-(methylthio)-benzyloxy]-1-butylhalide, 3-[4-(dimethylamino)-benzyloxy]-1-propylhalide, 6-[4-(dimethylamino)-benzyloxy]-1-hexylhalide, 4-(1-propyloxy)-1-butylhalide, 4-(1-methylethoxy)-1-butylhalide, 3-(triphenylmethoxy)-2,2-dimethyl-1-propylhalide, 4-(triphenylmethoxy)-1-butylhalide, 5-(triphenylmethoxy)-1-pentylhalide, 6-(triphenylmethoxy)-1-hexylhalide, 8-(triphenylmethoxy)-1-octylhalide, 3-(1,1-dimethylpropyloxy)-1-propylhalide, 3-(1,1-dimethylpropyloxy)-2,2-dimethyl-1-propylhalide, 4-(1,1-dimethylpropyloxy)-1-butylhalide, 6-(1,1-dimethylpropyloxy)-1-hexylhalide, 4-methoxy-1-butylhalide, 3-methoxy-1-butylhalide, 3-(triphenylmethoxy)-1-propylhalide, and 3-(1,1-dimethylpropyloxy)-2-methyl-1-propylhalide.

4. The process of claim 3 characterized in that the halide is selected from the group consisting of bromine and chlorine.
5. The process of claim 1 characterized in that the alkali metal is lithium.
6. A process for the anionic polymerization of an anionically polymerizable monomer characterized by the steps of:
 - a) initiating polymerization of a conjugated polyene hydrocarbon having 4 to 30 carbon atoms or a vinylsubstituted aromatic hydrocarbon in

a hydrocarbon or mixed hydrocarbon-polar solvent media at a temperature of 10-70°C with an initiator having the formula



- wherein M is defined as an alkali metal, selected from the group consisting of lithium, sodium and potassium; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, and R¹, R² and R³ are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups to produce an intermediate polymer and
- b) reacting the intermediate polymer with a functionalizing compound to produce a functionalized polymer
 - c) optionally hydrogenating the functionalized polymer
 - d) further reacting the functionalized polymer with one or more comonomers in the presence of a strong acid catalyst to simultaneously deprotect the polymer and polymerize the comonomers at both functional sites or
 - e) further reacting the functionalized polymer with other comonomers in the absence of strong acid catalysts, then deprotecting the resultant copolymer and
 - f) further reacting the resultant copolymer with the same or other comonomers
7. The process of claim 6 further characterized by reacting the intermediate polymer with a compound selected from the group consisting of ethylene oxide, carbon dioxide, 1,5-diazabicyclo (3.1.0) hexane, N-benzylidene trimethylsilylamide, sulfur, an omega-alkenylarylhalosilane, an isomeric divinylbenzene, a chlorosilane and dimethyldichlorosilane, and a chlorostannane and dibutyltin dichloride and recovering a functionalized linear or branched polymer having one or more terminal functional groups.
8. Hydrogenation of one or more recovered polymers of claim 7 to produce a hydrogenated polymer or polymers.
9. The process of claim 6 characterized in that the conjugated diene hydrocarbon is selected from the group consisting of 1,3-butadiene; isoprene; 2,3-dimethyl-1,3-butadiene; 1,3-pentadiene (piperylene), 2-

methyl-3-ethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, 1,3-hexadiene, 2,5-dimethylhexadiene and 1,3-octadiene.

10. The process of claim 6 characterized in that the polar solvent is selected from the group consisting of diethyl ether, triethylamine, methyl
5 tert-butyl ether, dibutyl ether, and tributylamine.

11. The process of claim 7 further characterized by reaction of the polymers of claim 7 produced from isomeric divinyl benzenes and deprotection of the resulting polymer to yield star-branched polymers with hydroxy-terminated branches.

10 12. The process of claim 11 characterized in that the star-branched polymers are hydrogenated.

13. The process of claim 12 characterized by further reaction of the hydrogenated deprotected polymers of claim 12 with ethylene oxide and potassium alkoxides to produce hydrogels.

15 14. The process of claim 13 characterized by further reaction of the hydrogenated and deprotected polymers of claim 13 with acryloyl chloride and methacryloyl chloride

15. The process of claim 14 further characterized by reacting the polymers of claim 14 with alkyl acrylates, alkyl methacrylates and
20 dialkylacrylamides to produce hydrogels.

16. The process of claim 7 characterized in that the functionalizing compound is ethylene oxide, the functionalized polymer is hydrogenated, and the comonomers are selected from the group of epichlorohydrin and diisocyanates to produce epoxide and isocyanate-terminated polymers.

25 17. The process of claim 16 further characterized by simultaneous deprotection and polymerization of the isocyanate and epoxy-terminated polymers .

18. The process of claim 7 further characterized by reaction of the hydrogenated polymer of claim 7 produced from ethylene oxide with
30 comonomers selected from the group consisting of dialkylterephthalates, alpha-omega alkane diols, diisocyanates caprolactam and adipic acid and the polymerization is carried out simultaneously with deprotection.

19. The process of claim 7 characterized in that the functionalizing compound is ethylene oxide, the comonomer is ethylene oxide, the
35 polymerization is carried out in the presence of potassium tert-butoxide,

the resulting copolymer is deprotected and reaction with comonomer continued.

20. The process of claim 7 characterized in that the functionalizing compound is ethylene oxide, the functional polymer is hydrogenated and
5 reacted with a diisocyanate in a 2:1 ratio, further reacted with hydroxyethylacrylate in the presence of a basic catalyst, and deprotected to yield a macromonomer.

21. The process of claim 7 characterized in that the functionalizing compound is styrenyldimethylchlorosilane.

10 22. A functionalized polymer produced by a process characterized by the steps of:

a) initiating polymerization of a conjugated polyene hydrocarbon or an alkenylsubstituted aryl hydrocarbon having 4 to 30 carbon atoms in a hydrocarbon or mixed hydrocarbon-polar solvent media at a temperature
15 of 10-70 °C with an initiator having the formula



wherein M is an alkali metal, Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, and R¹, R² and R³ are
20 independently selected from alkyl, substituted alkyl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups to produce an intermediate polymer,

b) reacting the intermediate polymer with a functionalizing compound

25 c) optionally hydrogenating the polymer

d) further reacting the functionalized polymer with one or more comonomers in the presence of a strong acid to simultaneously deprotect and polymerize the functionalized polymer or

e) further reacting the functionalized polymer with comonomers in
30 the absence of a strong acid catalyst, followed by deprotection and further reaction with the comonomers

23. The polymer of claim 22 characterized in that the functionalizing compound is selected from the group of ethylene oxide, oxygen, sulfur, carbon dioxide, an omega-alkenylarylhalosilanes, a
35 chlosilane, a chlorostannane and isomeric divinylbenzenes.

24. The polymer of claim 23 characterized in that the conjugated diene hydrocarbon is selected from the group consisting of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-3-ethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, 1,3-hexadiene, 2,5-dimethyl-2,4-hexadiene and 1,3-octadiene.

25. The polymer of claim 22 further characterized by the step of hydrogenating the polymerized conjugated polyene hydrocarbon

26. The polymer produced by the process of claim 12
27. The polymer produced by the process of claim 13
10 28. The polymer produced by the process of claim 14
29. The polymer produced by the process of claim 15
30. The polymer produced by the process of claim 16
31. The polymer produced by the process of claim 17
32. The polymer produced by the process of claim 18
15 33. The polymer produced by the process of claim 19
34. The polymer produced by the process of claim 20
35. The polymer produced by the process of claim 21
36. Hydrocarbon solutions of monofunctional ether initiators of the following structure;

20
$$\text{M-Z-O-C(R}^1\text{R}^2\text{R}^3\text{)}$$

characterized in that M is an alkali metal; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; and R¹, R², and R³ are independently selected from hydrogen alkyl, substituted alkyl groups
25 containing lower alkoxy, lower alkylthio, and lower dialkylamino groups, aryl, or substituted aryl groups containing lower alkoxy, lower alkylthio, and lower dialkylamino groups.

37. The monofunctional ether initiators of claim 36 characterized in that M is lithium, Z is a straight chain hydrocarbon tether containing 3
30 carbon atoms, and R¹, R², and R³ are methyl groups.

38. The monofunctional ether initiators of claim 36 characterized in that M is lithium, Z is a straight chain hydrocarbon group containing 4 carbon atoms, and R¹, R², and R³ are methyl groups.

39. The monofunctional ether initiators of claim 36 characterized in that M is lithium, Z is a straight chain hydrocarbon group containing 6 carbon atoms, and R¹, R², and R³ are methyl groups.

40. The monofunctional ether initiators of claim 36 characterized
5 in that M is lithium, Z is a straight chain hydrocarbon tether containing 8 carbon atoms, and R¹, R², and R³ are methyl groups.

41. The monofunctional ether initiators of claim 36 characterized in that M is lithium, Z is a straight chain hydrocarbon tether containing 3 carbons, and R¹ and R² are methyl groups and R³ is an ethyl group.

INTERNATIONAL SEARCH REPORT

In. ational application No.
PCT/US96/07625

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 4/46, 8/06, 8/10, 8/12, 8/34, 297/04
US CL : 502/157; 525/194, 314, 316, 332.9, 333.1, 333.3, 333.5
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 502/157; 525/194, 314, 316, 332.9, 333.1, 333.3, 333.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN-structure search, APS
search terms: butyllithium, propyllithium, alkylolithium, dimethyletoxy, methylethoxy, triphenylethoxy

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| A | Tetrahedron, Volume 41, No. 24, issued 1985, Gardette et al, "Carbocupration of Alkynes by Organocopper Reagents Bearing a Protected Hydroxy or Thiol Function", pages 5887-5899. | 1-5 and 36-41 |
| A | US, A, 4,753,991 (BRONSTERT) 28 June 1988. | 6-35 |
| Y | US, A, 3,862,100 (HALASA ET AL) 21 January 1975, the entire document. | 1-41 |
| A | US, A, 3,719,730 (HANSLEY ET AL) 06 March 1973, column 2, lines 10-33. | 6-35 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | |
|---|--|
| * Special categories of cited documents: | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| "A" document defining the general state of the art which is not considered to be of particular relevance | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| "E" earlier document published on or after the international filing date | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "G" document member of the same patent family |
| "O" document referring to an oral disclosure, use, exhibition or other means | |
| "P" document published prior to the international filing date but later than the priority date claimed | |

| | |
|---|---|
| Date of the actual completion of the international search 29 AUGUST 1996 | Date of mailing of the international search report 17 SEP 1996 |
| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230 | Authorized officer IRINA ZEMEL Telephone No. (703) 308-2351 |

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/07625

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/07625

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1-5, drawn to a process of preparation of hydrocarbon solution of a monofunctional initiator.
- II. Claims 6-21, drawn to a process of anionic polymerization.
- III. Claims 22-35, drawn to a functionilized polymer.
- IV. Claims 36-41, drawn to hydrocarbon solution of a monofunctional initiator.

The inventions listed as Groups I-IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature of the Group I, namely, the specific particle size of three specific alkali metals is not reflected or required in any of the Groups II-IV.